Description of Dynamic Properties of Finite Electron Systems in Density Functional Theory

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Abstract

The self consistent version of the density functional theory (DFT) is presented, which allows to calculate the ground state and dynamic properties of finite multi-electron systems such as atoms, molecules and clusters. The exact functional equation for the effective interaction, using which one can construct the action functional, density functional, the response functions, and excitation spectra of the considered systems, are discussed. We have also related the eigenvalues of the single-particle Kohn-Sham equations to the real single-particle spectra. We begin with the standard action functional and show that it is useful in calculating the linear response functions χ via which all physical characteristics of a many-body system can be expressed. It is shown, that function χ can be causal (retarded), noncausal and advanced ones. This resolves the well known paradox related to the causality and symmetry properties of the response functions and the effective interaction.

INTRODUCTION

The density functional theory (DFT) originated from the pioneer work of Hohenberg and Kohn [1] about thirty five years ago. Since then an impressive progress has been achieved by using DFT in describing microscopic many-particle systems and especially in studying multi-electron objects, such as atoms, molecules clusters and fullerenes. The recognition of DFT successes

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culminated in awarding W. Kohn the Nobel Price in Chemistry in 1998. At the beginning DFT was limited to consideration of only the ground state properties of many-particle systems, leaving aside their dynamic properties, which are closely related to the system's behavior in the time-dependent external fields. This limitation of DFT was overcome by Runge and Gross [2] who thus have transformed DFT into the so-called time-dependent density functional theory (TDDFT). Both, DFT and TDDFT are based on the one-to-one correspondence between the particle densities of the considered systems and external potentials acting upon these particles. For the sake of simplicity and definiteness, we assume that the time dependent part of the considered electronic system's density $\rho(\mathbf{r}, t)$, which is created under the action of an external time-dependent field $\lambda v_{ext}(\mathbf{r}, t)$, is developing from the system's ground state. As consequence of it one can conclude that each observable, describing the system, can be written as a functional of the density, among them are the functionals of the ground state energy $E[\rho]$ and of the action $A[\rho]$ [1, 2]. Then DFT and TDDFT establish an exact correspondence between an interacting many-body system and a fictitious non-interacting Kohn-Sham system [1, 2, 3]. The main advantage of the mapping is that Kohn-Sham system is described by a system of Hartree-type single particle equations, which is not too difficult to solve. As a result, after solving these equations in the case of an external time-independent potential, one can obtain and predict, at least in principle, the atomic, molecular, cluster and solid bodies binding energies, phonon spectra, activation barriers, and etc (see e.g. [1]). The same is true in the case of a time-dependent potential when the solution, generally speaking, yields the single-particle and collective excitation spectra, describes the behavior of a system in strong external fields, including that of atoms in short laser pulses (see e.g. [3, 4]). Unfortunately, the one-to-one correspondence establishes only the existence of the functionals in principle, leaving aside a very important question: how one can construct them in reality. This is why the success of DFT and TDDFT strongly depends upon the availability of good approximations for the functionals. As such, an approach based on the local density approximation and on numerical simulations of the ground state energy of a homogeneous in density electron system was suggested already in [1]. However the real molecules or atoms are not homogeneous and numerical simulations are not universally good. So, both justification and improvement of this approximation is required. But attempts to do it run into hard problems. They had to be overcome and it is highly desirable to find a systematic way to construct the required functionals. On the other hand, an important element of DFT, which is the action functional $A[\rho]$, is suspected to be ill-defined because of a number of contradictions in it. Perhaps the most important among them is the contradiction, which came from the analysis of the causality in TDDFT. It appeared, that this contradiction play a central role in creating a number of other difficulties [3, 5, 6]. In fact, it signals the existence of a very serious paradox: on one hand, according to the Runge-Gross theorem [2] $A[\rho]$ is a well defined functional, while on the other hand, the use of this functional

leads to fundamental difficulties.

Here we report some recent developments in eliminating this paradox. As we shall see, the methods used in resolving it give a good opportunity to construct equations defining the functionals $A[\rho]$, $E[\rho]$ and related to them effective interaction and the linear response function. Thus, this Comment will focus on formulating such an approach to the self-consistent density functional theory, that is based not only on the theorems of the existence of the functionals but also on the exact equations for them.

We will start with discussion of the paradox and show how it is eliminated, then go to single particle potentials, present the functional equations for the energy and action, derive the expression for the effective inter- electron interaction and illustrate the effectiveness of the suggested scheme.

It will be demonstrated that the presented approach is at the same time rather simple, as compared to the usual, say, diagram many-body technique, and offers a possibility to calculate relatively easy all the required characteristics of any multi-electron systems.

SYMMETRY AND CAUSALITY

Let us start with the discussion of the action functional $A[\rho]$, which is of key importance for the subject of this paper, because it permits to express the reaction of the many-body system under consideration to an external field. Due to the existence of one-to-one correspondence between the external potential $\lambda v_{ext}(\mathbf{r}, t)$ [2] and the time-dependent density $\rho(\mathbf{r}, t)$, the external potential determines also the time-dependent wave function $\phi[\rho](t)$ of the system in question. Therefore, the expectation value of any quantum mechanical operator is a unique functional of the density . This statement is also true for the action functional $A[\rho]$, which is determined by the expression [2, 3],

$$A[\rho] \;=\; \int_{t_i}^{t_f} dt \langle \phi(t)[\rho] \left| i\frac{\partial}{\partial t} - \hat{H}(t) \right| \phi(t)[\rho] \rangle. \tag{1}$$

The values of t_i and t_f can be chosen arbitrarily, we take $t_i = -\infty; t_f = +\infty$. The time-dependent wave function $\phi(t)$, which corresponds to a stationary point of the action functional (1), is a solution of the Schrödinger equation,

$$i\frac{\partial}{\partial t}\phi(t) = \hat{H}(t)\phi(t),$$

with the hamiltonian, that we present as a sum of two terms,

$$\hat{H}(t) = \hat{H} + \hat{H}_1(t). \tag{2}$$

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Here $\hat{H} = \hat{K} + \hat{V}$ acting alone describes the ground state of the considered system, while $\hat{H}_1(t)$ represents the external field and is given by the following expression:

$$\hat{H}_1(t) = \int \hat{\rho}(\mathbf{r}) \lambda v_{ext}(\mathbf{r}, t) d\mathbf{r}.$$

Here $\hat{\rho}(\mathbf{r})$ is the electron density operator. The operator $\hat{K}$ is the hamiltonian of non-interacting particles and $\hat{V}$ represents the two-particle Coulomb interaction. Upon using eqs. (1,2) the functional $A[\rho]$ can be presented as,

$$A[\rho] = A_1[\rho] - \int \lambda v_{ext}(\mathbf{r}, t) \rho(\mathbf{r}, t) d\mathbf{r} dt, \tag{3}$$

with $A_1 = A|_{\lambda=0}$ being a universal functional of the considered system, which is explicitly independent upon the external field. Using the action functional A_1, it is possible to construct the inverse of the linear response function χ, i.e. χ^{-1}, [4],

$$\chi^{-1}(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2) = \frac{\delta^2 A_1[\rho]}{\delta\rho(\mathbf{r}_1, t_1)\delta\rho(\mathbf{r}_2, t_2)}. \tag{4}$$

One needs to know the function χ, because all characteristics of a many-particle system are expressed via it. From eq. (4) it might seem as self evident, that not only χ^{-1} but also the direct linear response function χ defined by $\chi^{-1}(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2)$ must be a symmetrical function of its space and time arguments [3, 5, 6]. However, χ, being symmetric under interchange of $(\mathbf{r}_1, t_1)$ and $(\mathbf{r}_2, t_2)$, cannot be a causal function, while determined in the usual way $\chi(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2)$ is known to be a retarded (causal) function and, therefore, must vanish $t_2 > t_1$ [7, 8]. Therefore it was concluded that eq. (4) is incorrect [3, 5, 6], because the symmetry and causality looked as contradicting each other. To overcome this difficulty, it was suggested that the problem is related to the boundary conditions $\delta\phi(t_i) = \delta\phi(t_f) = 0$ which one has to enforce on the variation of the wave function while deriving the time-dependent Schrödinger equation from eq. (1). It was argued, that since the action functional is defined only on the sufficiently narrow domain of v-representable (VR) wave functions and densities, the condition $\delta\phi(t_f) = 0$ cannot be fulfilled. The v-representability means that the wave functions and corresponding densities are solutions of the Schrödinger equation with an external potential $v(\mathbf{r}, t)$ [1, 9]. Thus, a non-vanishing boundary term appears when the variation δA is made. Therefore, it was recommended to search for another functional to avoid the mentioned above causality-symmetry problems [6]. But, as it was demonstrated above, the existence of the action functional is guaranteed by the Runge-Gross theorem [2], which play the key role in establishing TDDFT. As a result, the paradox has thrown doubt on the reliability of TDDFT and it became crucially important to resolve it.

In eliminating this paradox, we shall follow the papers [4, 10]. Consider a stable multi-electron system evolving from its ground state ϕ_0 with the density ρ_0 under the influence of a weak external potential λv_{ext}, that is in the limit $\lambda \to 0$. This condition prevents the system under consideration from a steady heating, ensuring the existence of the linear response function χ as well as its inverse χ^{-1} [7, 8]. For such a system all the densities and wave functions in the vicinity of the ground state are VR including those which satisfy the boundary conditions [9, 11, 12]. Therefore the correct time-dependent density can be obtained from the Euler equation [2],

$$\frac{\delta A[\rho]}{\delta \rho(\mathbf{r}, t)} = 0. \tag{5}$$

It is worth to note, that this equation is more general than the boundary condition. It means that (5) can be correct even if $\delta\phi(t_f) \neq 0$. Now we can use (5) to prove (4). According to (3), the Euler equation (5) can be written in the following form,

$$\frac{\delta A[\rho]}{\delta \rho(\mathbf{r}, t)} = \frac{\delta A_1[\rho]}{\delta \rho(\mathbf{r}, t)} - \lambda v_{ext}(\mathbf{r}, t) = 0. \tag{6}$$

To prove (4), we expand the solution of (6) in terms of the density fluctuations $\delta\rho = \rho_1 - \rho_0$, induced by the external field:

$$\frac{\delta A_1}{\delta \rho}\Big|_{\rho_0} + \frac{\delta^2 A_1}{\delta \rho^2}\Big|_{\rho_0} \delta\rho - \lambda v_{ext}\Big|_{\lambda \to 0} = 0, \tag{7}$$

where ρ_1 is the density in the presence of λv_{ext}. The first term in (7) vanishes because of the stationary condition (5). Upon using the definition of the linear response function $\chi = \delta\rho/\delta\lambda v_{ext}$, the exact equation is obtained [4],

$$\chi^{-1}(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2) = \frac{\delta^2 A_1[\rho]}{\delta \rho(\mathbf{r}_1, t_1)\delta \rho(\mathbf{r}_2, t_2)}\Big|_{\lambda=0}. \tag{8}$$

Thus, we come to the conclusion that the second functional derivative of the action integral A_1 appeared in eq. (8) defines and is defined by the inverse of the linear response function, which, as it should be, is a symmetrical function of its variables. To understand the physical meaning of eq. (8), which defines a symmetrical function χ^{-1}, consider eq. (1) which determines the action A. It is known that by varying this equation with respect to ϕ^* one derives the Schrödinger equation for the retarded solution ϕ, $\phi_r(\mathbf{r}, t)$, while the variation with respect to ϕ leads to the advanced solution ϕ^*, $\phi_a^*(\mathbf{r}, -t)$. As a result, the variation of the action functional with respect to the density ρ produces a superposition of the advanced and retarded solutions. This is why eq. (8) defines a symmetrical function. Now we are going to demonstrate that having the

noncausal function χ^{-1}, it is possible to construct any type of the linear response functions χ: noncausal, and causal (both retarded and advanced) linear response functions. The response function χ is connected to its inverse by the following relation:

$$\delta(t_1 - t_3)\delta(\mathbf{r}_1 - \mathbf{r}_3) = \int_{\tau_1}^{\tau_2} \chi^{-1}(\mathbf{r}_1, \mathbf{r}_2, t_1, t_2)\chi(\mathbf{r}_2, \mathbf{r}_3, t_2, t_3)d\mathbf{r}_2 dt_2, \tag{9}$$

We see that noncausal χ^{-1} is the kernel of the integral equation (9). The character of solutions χ obtained from (9) depends on the boundary conditions which are defined by numbers τ_1 and τ_2. If the linear response function has to be causal, that is to be nonzero only at $t_2 \geq t_3$ then $\tau_1 = t_3$ and $\tau_2 = \infty$. If noncausal χ is required, then $\tau_1 = -\infty$ and $\tau_2 = \infty$, while in the case of advanced χ it has to be $\tau_1 = -\infty$, and $\tau_2 = t_3$. As we will see below, using a different way, the linear response function may be chosen indeed causal, noncausal or advanced. And vice versa, starting, for instance, with the causal linear response function χ, taken as the kernel of (9), one can construct χ^{-1} of desirable kind using the same eq. (9) and choosing the appropriate boundary conditions. Thus, we come to the conclusion: it is the existence of the symmetrical (noncausal) inverse χ^{-1} that leaves no room for the paradox [4, 10]. Note that the particular case when χ^{-1} is noncausal while χ is causal has been studied [13] recently.

It is worth to consider in more details the case when both χ and χ^{-1} are causal since one may suspect that there are no such solutions of (9) [13]. To show that the causal function χ_r^{-1} does exist we consider the well known definition of the linear response function,

$$\delta\rho(\mathbf{r}_1, t_1) = \int_0^{t_1} \chi(\mathbf{r}_1, \mathbf{r}_2, t_1, t_2)\lambda\hat{q}(\mathbf{r}_2)v(t_2)d\mathbf{r}_2 dt_2. \tag{10}$$

For simplicity we substitute the external field in eq. (10) by $v_{ext}(\mathbf{r}, t) = \lambda\hat{q}(\mathbf{r})v(t)$. Then, eq. (10) transforms into Volterra's integral equation of the first kind, which always has a solution, see e.g. [14]. Thus, we conclude that the causal inverse χ_r^{-1} exists.

In order to demonstrate that one can use the causal (retarded), advanced and noncausal linear response functions equally effective let us consider the second functional derivative of the action with respect to external field. Because of the one-to-one correspondence between external potential $\lambda v_{ext}(\mathbf{r}, t)$ and time dependent density $\rho(\mathbf{r}, t)$ such a functional $A_1[v]$ exists. Then, taking into account that the inverse of the linear response χ is given by $\delta\lambda v_{ext}/\delta\rho = \chi^{-1}$ and using (8), one obtains,

$$\chi(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2) = \frac{\delta^2 A_1[v]}{\delta\lambda v_{ext}(\mathbf{r}_1, t_1)\delta\lambda v_{ext}(\mathbf{r}_2, t_2)}|_{\lambda=0}. \tag{11}$$

It is useful to derive eq. (11) directly from the definition (1). We restrict ourselves to an infinitesimally weak time-dependent field putting $\lambda = 0$ after completing the calculations.

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Therefore the usual many-body technique of diagrams can be applied in calculating the variational derivatives with respect to the external field [15, 16]. The variation ΔA_1 of the action $A_1[v]$ induced by the time-dependent external field is then defined as,

$$\Delta A_1 = \int_{t_i}^{t_f} dt \langle \phi(t) | i\frac{\partial}{\partial t} - \hat{H} | \phi(t) \rangle = \int_{t_i}^{t_f} dt \frac{< \phi_0 | T(\hat{H}_{\tau 1}(t)S(\infty))|\phi_0 >}{< \phi_0 | T(S(\infty))|\phi_0 >}, \tag{12}$$

where T is the usual time-ordering operator, and $\hat{H}_{\tau 1}(t)$ is $\hat{H}_1(t)$ in the interaction representation with respect to the hamiltonian $\hat{H}$. The expression for $S(\infty)$ is defined by the following way,

$$S(\infty) = T \exp\left[-i \int_c \hat{H}_{\tau 1}(t)dt\right], \tag{13}$$

where c is the contour of integration, which starts at $-\infty$ and ends at $+\infty$. Note that the functional $A_1[v]$ formally defined as,

$$A_1[v] = i \ln < \phi_0 | T(S(\infty))|\phi_0 >, \tag{14}$$

will give the variation ΔA_1 with respect to the external field, which coincides with the variation following from eq. (14). Calculating the second variational derivative of A_1 given by eq. (14) with respect to the external field λv_{ext} and putting $\lambda = 0$ in the final result, one gets the following relation:

$$\frac{\delta^2 A_1[v]}{\delta \lambda v_{ext}(\mathbf{r}_1, t_1)\delta \lambda v_{ext}(\mathbf{r}_2, t_2)} \mid_{\lambda=0} = \chi(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2) \tag{15}$$

$$= -i(< \phi_0 | T\rho(\mathbf{r}_1, t_1)\rho(\mathbf{r}_2, t_2) | \phi_0 > - < \phi_0 | \rho(\mathbf{r}_1, t_1) | \phi_0 >< \phi_0 | \rho(\mathbf{r}_2, t_2) | \phi_0 >).$$

It is seen from eq. (15) that the second functional derivative of the action integral A_1 with respect to the external field is defined by the noncausal linear response function, which, as it should be, is a symmetrical function of its variables [4]. After performing the Fourier transformation with respect to time, $\chi(\mathbf{r}_1, \mathbf{r}_2, \omega)$ takes the form,

$$\chi = \sum_{k\neq 0} \left[\frac{< 0 | \hat{\rho}^\dagger(\mathbf{r}_1) | k >< k | \hat{\rho}(\mathbf{r}_2) | 0 >}{\omega - (E_k - E_0) + i\delta} - \frac{< 0 | \hat{\rho}^\dagger(\mathbf{r}_2) | k >< k | \hat{\rho}(\mathbf{r}_1) | 0 >}{\omega + (E_k - E_0) - i\delta} \right]. \tag{16}$$

Here $| 0 >$, E_0 and $| n >$, E_k are the many-particle system's exact ground and excited state wave functions and energies, respectively. It is evident from (16) that χ has poles in II and IV quadrants of the complex ω plane. It contains exactly the same information related to the properties of a system as the causal linear response function, while both these functions coincide on the imaginary axis of the plane, being related one to another by analytical continuation

[8, 16]. Just in the same way the response functions of higher orders can be constructed. So, having at hand the action $A_1[\rho]$, one can study the ground and excited states of a system. Thus, eq. (8) is of key importance in calculations of the excited states within the TDDFT framework [4]. Note, that eq. (8) was later verified in [20]. It is pertinent to point here that one can use the non-equilibrium Green function theory [17, 18] to construct both the retarded (causal) linear response function χ_r, which has poles in the III and IV quadrants, and the advanced linear response function χ_a, with poles being in the I and II quadrants. The only formal difference from the used above technique is the appearance of the counter ordered evolution operator T_{cr} instead of the usual time-ordering operator T [18]. Thus we can use eq. (14) to evaluate $A_1[v]$ replacing T by T_{cr}, in this case eq. (14) is modified as,

$$A_1[v] = i \ln < \phi_0|T_{cr}(S(\infty))|\phi_0 >, \tag{17}$$

with T_{cr} being the contour-ordering operator, which orders the operators along the contour cr according to the position on the counter of their time arguments. Then, upon using eq. (17), we have instead of eq. (15),

$$\frac{\delta^2 A_1[v]}{\delta \lambda v_{ext}^2} \big|_{\lambda=0} = \chi_r(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2) = -i\theta(t_1 - t_2) < \phi_0 \mid [\rho(\mathbf{r}_1, t_1)\rho(\mathbf{r}_2, t_2)] \mid \phi_0 > . \tag{18}$$

Here the brackets [...] denote the commutator of the density operators. In the same way as χ_r was constructed, one can get the advanced linear response function χ_a, choosing a special contour ca along which the contour-ordering operator T_{ca} orders the operators. Thus, different forms of linear response functions correspond simply to different choices of the contours. This result is quite obvious: if one marks the moment on the contour then it is possible to construct the retarded (advanced) linear response function, using eq. (17) for the action functional. If no moment of time is marked along the contour, and we deal with the original action functional given by eq. (14), we shall have the linear response function χ defined by eq. (15) in accordance with the previous discussion. Thus, we can conclude that functional A is in fact well defined, while eq. (4), which determines the inverse function χ^{-1}, opens the possibility to calculate the dynamic properties of a system including its excitation spectra [4, 19, 20].

SINGLE PARTICLE POTENTIAL

Now let us construct the single particle potential $v_s[\rho](\mathbf{r}, t)$ of the time-dependent Kohn-Sham equations. It is convenient to define the exchange-correlation functional A_{xc} [2, 3],

$$A_{xc}[\rho] \equiv A_0[\rho] - A_1[\rho] - \frac{1}{2} \int \frac{\rho(\mathbf{r}_1, t)\rho(\mathbf{r}_2, t)}{|\mathbf{r}_1 - \mathbf{r}_2|} dt \, d\mathbf{r}_1 d\mathbf{r}_2, \tag{19}$$

in atomic units, used throughout this paper. Here A_0 is the functional of non-interacting Kohn-Sham particles,

$$A_0[\rho] = \int_{t_i}^{t_f} dt \langle \Phi(t)[\rho] \left| i\frac{\partial}{\partial t} - \hat{K} \right| \Phi(t)[\rho] \rangle,$$

with $\Phi(t)[\rho]$ being the unique time-dependent Slater determinant of the density ρ [2, 3]. The effective interaction $R^{(0)}$ is defined as [4, 19, 21],

$$R^{(0)}(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2) \equiv \frac{\delta(t_1 - t_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{\delta^2 A_{xc}}{\delta\rho(\mathbf{r}_1, t_1)\delta\rho(\mathbf{r}_2, t_2)}. \tag{20}$$

Combining eqs. (8) and (20), the effective interaction $R^{(0)}(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2)$ is determined by the relation,

$$R^{(0)}(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2) = \chi_0^{-1}(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2) - \chi^{-1}(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2), \tag{21}$$

where $\chi_0^{-1} = \delta^2 A_0/\delta\rho^2$ is the inverse of the linear response function of non-interacting Kohn-Sham particles. In the same way, calculating the functional derivatives of higher orders, one can obtain the effective interaction $R^{(l)}$, $l \geq 2$,

$$R^{(l)}(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2, ...\mathbf{r}_{l+2}, t_{l+2}) = \frac{\delta^{l+2} A_{xc}[\rho]}{\delta\rho(\mathbf{r}_1, t_1)\delta\rho(\mathbf{r}_2, t_2)...\delta\rho(\mathbf{r}_{l+2}, t_{l+2})} |_{\lambda=0} . \tag{22}$$

Then, taking the Fourier transform of the effective interaction with respect to time, making the analytical continuation to obtain the causality, and upon carrying out the inverse Fourier transform, one can get the causal effective interaction terms $\Re^{(l)}$. These terms $\Re^{(l)}$ are members of a series, which define the causal effective interaction $\Re[\rho]$,

$$\Re[\rho](\mathbf{r}_1, t_1, \mathbf{r}_2, t_2) \tag{23}$$

$$= \sum_{l\geq 0} \int \frac{1}{l!} \Re^{(l)}(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2, ...\mathbf{r}_{l+2}, t_{l+2})\delta\rho(\mathbf{r}_3, t_3)...\delta\rho(\mathbf{r}_{l+2}, t_{l+2})d\mathbf{r}_3 dt_3...d\mathbf{r}_{l+2} dt_{l+2}.$$

Having at hand $\Re$, one can construct the single-particle potential $v_s[\rho](\mathbf{r}, t)$ by integrating the equation, which determines this potential

$$\frac{\delta v_s[\rho](\mathbf{r}_1, t_1)}{\delta\rho(\mathbf{r}_2, t_2)} = \frac{\delta v_{xc}[\rho](\mathbf{r}_1, t_1)}{\delta\rho(\mathbf{r}_2, t_2)} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \Re[\rho](\mathbf{r}_1, t_1, \mathbf{r}_2, t_2), \tag{24}$$

with v_{xc} being the exchange-correlation potential. Eq. (24) can be integrated as simple as one can integrate the Tailor expansion of a function,

$$v_s[\rho](\mathbf{r}_1, t_1) = \int \Re^{(0)}(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2)\delta\rho(\mathbf{r}_2, t_2)d\mathbf{r}_2 dt_2 \tag{25}$$

$$+\sum_{l\geq 1}\int\frac{1}{(l+1)!}\Re^{(l)}(\mathbf{r}_1,t_1,\mathbf{r}_2,t_2,...\mathbf{r}_{l+2},t_{l+2})\delta\rho(\mathbf{r}_2,t_2)...\delta\rho(\mathbf{r}_{l+2},t_{l+2})d\mathbf{r}_2dt_2...d\mathbf{r}_{l+2}dt_{l+2}.$$

Then, one can use the exact functional equation for $R(\mathbf{r}_1,\mathbf{r}_2,\omega,g)$ [4, 19] to construct approximations to $v_s[\rho]$,

$$R(\mathbf{r}_1,\mathbf{r}_2,\omega,g)=\frac{g}{|\mathbf{r}_1-\mathbf{r}_2|}\tag{26}$$

$$-\frac{1}{2}\frac{\delta^2}{\delta\rho(\mathbf{r}_1,\omega)\delta\rho(\mathbf{r}_2,-\omega)}\int\int_0^g\chi(\mathbf{r}_1',\mathbf{r}_2',iw,g')\frac{1}{|\mathbf{r}_1'-\mathbf{r}_2'|}d\mathbf{r}_1{}'d\mathbf{r}_2{}'\frac{dw}{2\pi}dg'.$$

Here $R(\mathbf{r}_1,\mathbf{r}_2,\omega,g)$ is the effective interaction depending on the coupling constant g of the Coulomb interaction. The coupling constant g in eq. (26) is varied in the range $(0-1)$. When $g=1$ one has $R^{(0)}=R(g=1)$. In eq. (26) the linear response function $\chi(\mathbf{r}_1,\mathbf{r}_2,\omega,g)$ is the Fourier-image in (t_1-t_2) of the linear response function. It is obtained from eq. (21) through algebraic transformation and by introducing the coupling constant g,

$$\chi(\mathbf{r}_1,\mathbf{r}_2,\omega,g)=\chi_0(\mathbf{r}_1,\mathbf{r}_2,\omega)+\int\chi_0(\mathbf{r}_1,\mathbf{r}_1',\omega)R(\mathbf{r}_1{}',\mathbf{r}_2{}',\omega,g)\chi(\mathbf{r}_2',\mathbf{r}_2,\omega,g)d\mathbf{r}_1'd\mathbf{r}_2',\tag{27}$$

with χ_0 being the linear response function of non-interacting Kohn-Sham particles, moving in the single-particle time-independent field [4, 19]. It is evident that the linear response function $\chi(g=1)$ goes to χ as g goes to 1.

The physical meaning of (25) is quite transparent: as it is seen from (24,25), the functions $\Re^{(l)}$ are directly obtained by calculating the corresponding functional derivatives of $v_s[\rho]$ with respect to the density. This shows that the single particle time-dependent potential contains a lot of information about the system. And, vise versa, to construct $v_s[\rho]$ one needs the same information. It is important to note that $v_s[\rho]$, determined by eq. (25), is suitable to describe the system in a strong external field due to the general property, given by eq. (3), with the provision that the series in eq. (25) is convergent.

It is instructive to consider eqs. (8,15) in the case when external field λv_{ext} is not weak. Deriving (8,15), we used the fact that the linear response function and its inverse exist when $\lambda=0$. In the case when $\lambda=\lambda_0\neq 0$, the existence of both of these functions is not self-evident. Moreover, it is quite probable that in the general case their existence is impossible to prove. The behavior of a system in an arbitrary (including the strength) time-dependent field may be very complicated and unstable, for instance, due to a permanent transfer of the energy from the external field to the system under consideration. On the other hand, the non-equilibrium theory is fitted to describe time-dependent steady states, it is those states that are stable against small perturbations [17]. But stability against small perturbations means that there exist the response function of the system under consideration and its inverse function. So let us suppose

the existence of both of these functions. This can be correct provided the series in eq. (25) are convergent. Under this condition we can apply the same consideration that has been used when deriving eqs. (8,15): the density of the system imbedded in the external field is VR, then the densities in the neighborhood are also VR [11]. As the result, the action functional $A[\rho]$ is defined, and eq. (5) is valid. One can also apply eq. (7) to prove (8), having in mind that $\lambda \to \lambda_0$, while ρ_0 in the considered case is the time-dependent density in the external field $\lambda_0 v_{ext}$. On the other hand, we can use eq. (17) evaluating $A_1(\lambda_0)$, which is correct in the presence of an external field. The symbol (λ_0) emphasizes that the external field is not a weak one. As a consequence, we obtain the retarded response function $\chi_r(\lambda_0)$, given by eq. (17). The advanced response function $\chi_a(\lambda_0)$ is defined in the same manner by choosing the contour ca. The contour, which starts at $-\infty$ and ends at $+\infty$, will produce the response function $\chi(\lambda_0)$. Thus, we are coming to the conclusion that the standard definition of the action functional (1), as well as eqs. (8,15,17,18) are also valid in the considered case of a strong external field. Further investigation of the behavior of a system in this case will be published elsewhere.

EQUATIONS

In this section we briefly outline the derivation of the functional equation for the exchange-correlation functionals E_{xc} and A_{xc} when system in question does not perturbed by an external field. In that case one has

$$E_{xc}[\rho] = A_{xc}[\rho]|_{\rho(r,\omega=0)}, \tag{28}$$

since A_{xc} is also defined in the static densities domain. The exchange-correlation functional may be obtained from [4, 19]:

$$A_{xc} = -\frac{1}{2} \int \left[\chi(\mathbf{r}_1, \mathbf{r}_2, iw) + 2\pi\rho(\mathbf{r}_1)\delta(w)\delta(\mathbf{r}_1 - \mathbf{r}_2) \right] \frac{g'}{|\mathbf{r}_1 - \mathbf{r}_2|} \frac{dg'}{g'} \frac{dw}{2\pi} d\mathbf{r}_1 d\mathbf{r}_2. \tag{29}$$

Eq. (29) presents the well-known expression for the exchange-correlation energy of a system, see e.g. [4, 7, 19]. The only thing we need, in order to consider eq. (29) as describing A_{xc}, is an ability to calculate the functional derivatives of A_{xc} with respect to the density. This, as it is seen from eq. (29), reduces to the ability of calculating the functional derivatives of the linear response function χ with respect to the density $\rho(\mathbf{r}, \omega)$ which was developed in [19, 22]. Then the linear response function is given by (27), and the effective interaction R is defined by the exact functional (26). The single-particle potential v_{xc}, being time-independent, is of the form [4, 19],

$$v_{xc}(\mathbf{r}) = \frac{\delta}{\delta\rho(\mathbf{r}, t)} A_{xc}|_{\rho=\rho_0}. \tag{30}$$

Here the functional derivative is calculated at $\rho = \rho_0$ with ρ_0 being the equilibrium density. By substituting (29) into (30), it can be shown that the single particle potential v_{xc} has the proper asymptotic behavior, $v_{xc}(r \to \infty) \to -1/r$, [19, 23]. The potential v_{xc} determines the energies ε_i and wave functions ϕ_i of fictitious Kohn-Sham particles,

$$\left(-\frac{\nabla^2}{2} + V_H(\mathbf{r}) + V_{ext}(\mathbf{r}) + v_{xc}(\mathbf{r}) \right) \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}), \tag{31}$$

that in turn form the linear response function χ_0,

$$\chi_0(\mathbf{r}_1, \mathbf{r}_2, \omega) = \sum_{i,k} n_i(1 - n_k)\phi_i^*(\mathbf{r}_1)\phi_i(\mathbf{r}_2)\phi_k^*(\mathbf{r}_2)\phi_k(\mathbf{r}_1) \left[\frac{1}{\omega - \omega_{ik} + i\eta} - \frac{1}{\omega + \omega_{ik} - i\eta} \right], \tag{32}$$

and the real density of the system ρ,

$$\rho(\mathbf{r}) = \sum_i n_i |\phi_i(\mathbf{r})|^2. \tag{33}$$

Here n_i are the occupation numbers, V_{ext} contains all external single-particle potentials of the system, say the Coulomb potentials of the nuclei. Then, V_H is the Hartree potential,

$$V_H(\mathbf{r}) = \int \frac{\rho(\mathbf{r}_1)}{|\mathbf{r} - \mathbf{r}_1|} d\mathbf{r}_1,$$

and ω_{ik} is the one-particle excitation energy $\omega_{ik} = \varepsilon_i - \varepsilon_k$, while η being an infinitesimally small positive number. The described above equations (29-31) and (26,27) solve the problem of constructing the self-consistent DFT: one can calculate A_{xc}, the ground state energy and excitation spectra of a system without resorting to approximations for A_{xc} based on additional and foreign to the considered problem calculations such as Monte Carlo simulations, or something of this kind. We note, that using these approximations, one faces difficulties in constructing the effective interaction of finite radius and the linear response functions [3, 5]. On the base on the suggested approach one can solve these problems. For instance, in the case of a homogeneous electron liquid it is possible to determined analytically an efficient approximate expression R_{RPAE} for the effective interaction R, which essentially improves the well-known Random Phase Approximation [19, 21] by taking into account the exchange of electrons properly, thus forming the Random Phase Approximation with Exchange. The corresponding expression for R_{RPAE} is as follows

$$R_{RPAE}(q, g, \rho) = \frac{4\pi g}{q^2} + R_E(q, g, \rho), \tag{34}$$

where

$$R_E(q, g, \rho) = -\frac{g\pi}{p_F^2} \left[\frac{q^2}{12p_F^2} \ln \left| 1 - \frac{4p_F^2}{q^2} \right| - \frac{2p_F}{3q} \ln \left| \frac{2p_F - q}{2p_F + q} \right| + \frac{1}{3} \right]. \tag{35}$$

Here the electron density ρ is connected to the Fermi momentum by the ordinary relation $\rho = p_F^3/3\pi^2$. Having at hand the effective interaction $R_{RPAE}(q, g, \rho)$, one can calculate the correlation energy ε_c per electron of the electron gas with the density r_s. The dimensionless parameter $r_s = r_0/a_B$ is usually introduced to characterize the density, with r_0 being the average distance between electrons, and a_B is the Bohr radius. The density is high, when $r_s \ll 1$.

Table 1.　　　　　　　Correlation energy per electron in eV of an electron gas of density r_s. The Monte Carlo results [24] ε_c^M are compared with the RPA calculations and with the results of [21]. ε_{RPA} denotes the results of RPA calculations, and ε_{RPAE} denotes the results of the calculations when the effective interaction R was approximated by R_{RPAE} [21].

r_s	ε_c^M	ε_{RPA}	ε_{RPAE}
1	-1.62	-2.14	-1.62
3	-1.01	-1.44	-1.02
5	-0.77	-1.16	-0.80
10	-0.51	-0.84	-0.56
20	-0.31	-0.58	-0.38
50	-0.16	-0.35	-0.22

As can be seen from Table 1, the effective interaction $R_{RPAE}(q, \rho)$ permits to describe the electron gas correlation energy ε_c in an extremely broad interval of density variation. Note, that even at $r_s = 10$ the mistake is no more than 10% as compared to Monte Carlo calculations, while the result becomes almost exact at $r_s = 1$ and is absolutely exact when $r_s \to 0$ [21].

Now let us calculate the single particle energies ϵ_i, that, generally speaking, do not coincide with the eigenvalues ε_i of eq. (31). We remark that the eigenvalues do not make a physical sense, see e.g. [1]. To calculate the single particle energies one can use the Landau equation [8],

$$\frac{\delta E}{\delta n_i} = \epsilon_i. \tag{36}$$

Eq. (36) can be used since, as it follows from eqs. (27,32,33), the density and the linear response function depend upon the occupation numbers. Thus, one can consider the ground

state energy as a functional of the density and the occupation numbers, [25],

$$E[\rho(\mathbf{r}), n_i] = T_k[\rho(\mathbf{r}), n_i] + \frac{1}{2} \int V_H(\mathbf{r})\rho(\mathbf{r})d(\mathbf{r}) + \int V_{ext}(\mathbf{r})\rho(\mathbf{r})d(\mathbf{r}) + E_{xc}[\rho(\mathbf{r}), n_i]. \qquad (37)$$

Here T_k is the kinetic-energy functional of non-interacting Kohn-Sham particles. It follows from eqs. (29,31,36,37) that the single-particle energies ϵ_i can be presented by the following expression,

$$\epsilon_i = \varepsilon_i - <\phi_i|v_{xc}|\phi_i> -\frac{1}{2}\frac{\delta}{\delta n_i}\int \left[\frac{\chi(\mathbf{r}_1, \mathbf{r}_2, iw) + 2\pi\rho(\mathbf{r}_1)\delta(w)\delta(\mathbf{r}_1 - \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\right]\frac{dwdg'd\mathbf{r}_1 d\mathbf{r}_2}{2\pi}. \qquad (38)$$

Here, as it follows from (27), $\delta\chi/\delta n_i$ is given by the equation,

$$\frac{\delta\chi}{\delta n_i} = \frac{\delta\chi_0}{\delta n_i} + \frac{\delta\chi_0}{\delta n_i}R\chi + \chi_0\frac{\delta R}{\delta n_i}\chi + \chi_0 R\frac{\delta\chi}{\delta n_i}. \qquad (39)$$

In (39) for the sake of brevity we omit the spatial integrations. The variational derivative $\delta\chi_0/\delta n_i$ has the simple functional form,

$$\frac{\delta\chi^0(\mathbf{r}_1, \mathbf{r}_2, \omega)}{\delta n_i} = [G_0(\mathbf{r}_1, \mathbf{r}_2, \omega + \varepsilon_i) + G_0(\mathbf{r}_1, \mathbf{r}_2, -\omega + \varepsilon_i)]\,\phi_i^*(\mathbf{r}_1)\phi_i(\mathbf{r}_2), \qquad (40)$$

with $G_0(\mathbf{r}_1, \mathbf{r}_2, \omega)$ being the Green function of N non-interacting electrons moving in the single particle potential $V_H + v_{xc} + V_{ext}$. We believe and some evidences can be found in [4] that the contribution coming from $\delta R/\delta n_i$ is small. Nonetheless even having omitted this term, we are still to deal with rather involved eqs. (38,39). Therefore, it is of interest to illustrate the general consideration of the one-electron energies with a simple and important example, when only the exchange part A_x of the total exchange-correlation functional is selected to be treated rigorously, using an approximation for $A_c = A_{xc} - A_x$. Taking into account eq. (28) and the local density approximation, one gets,

$$E_c[\rho] = \int \rho(\mathbf{r})\varepsilon_c((\mathbf{r}))d\mathbf{r}. \qquad (41)$$

While for functional A_x we have an exact expression [19, 22],

$$A_x[\rho] = E_x[\rho] = -\frac{1}{2}\int [\chi_0(\mathbf{r}_1, \mathbf{r}_2, iw) + 2\pi\rho(\mathbf{r}_1)\delta(w)\delta(\mathbf{r}_1 - \mathbf{r}_2)]\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\frac{dw}{2\pi}d\mathbf{r}_1 d\mathbf{r}_2. \qquad (42)$$

As it is seen from eq. (30), single-particle potential v_{xc} takes from,

$$v_{xc}(\mathbf{r}) = v_x(\mathbf{r}) + v_c(\mathbf{r}), \qquad (43)$$

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with the potentials being given by,

$$v_x(\mathbf{r}) = \frac{\delta E_x}{\delta \rho(\mathbf{r})}; \ v_c(\mathbf{r}) = \frac{\delta E_c}{\delta \rho(\mathbf{r})}. \tag{44}$$

We remark that $v_x(\mathbf{r})$ can be calculated exactly [22, 26], while there are quite suitable approximations to the potential, see e.g. [27]. Presenting single-particle potential $v_{xc}(\mathbf{r})$ in such a way, we simplify the calculations a lot, preserving the mentioned above condition $v_{xc}(r \to \infty) \to -1/r$, which of crucial importance for calculations of ε_i related to the Kohn-Sham unoccupied states, see eq. (31). In the same way as eq. (38) was derived, one gets,

$$\epsilon_i = \varepsilon_i - < \phi_i|v_x|\phi_i > -\frac{1}{2}\frac{\delta}{\delta n_i} \int \left[\frac{\chi_0(\mathbf{r}_1, \mathbf{r}_2, iw) + 2\pi\rho(\mathbf{r}_1)\delta(w)\delta(\mathbf{r}_1 - \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \right] \frac{dw \, d\mathbf{r}_1 d\mathbf{r}_2}{2\pi}. \tag{45}$$

After straightforward calculations one arrives at rather simple result for the single-particle spectra, that are to be compared with experimental results,

$$\epsilon_i = \varepsilon_i - < \phi_i|v_x|\phi_i > -\sum_i n_k \int \left[\frac{\phi_i^*(\mathbf{r}_1)\phi_i(\mathbf{r}_2)\phi_k^*(\mathbf{r}_2)\phi_k(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} \right] d\mathbf{r}_1 d\mathbf{r}_2. \tag{46}$$

The single-particle levels ϵ_i, given by eq. (46), resemble the ones that are obtained within the Hartree-Fock (HF) approximation. If the wave functions ϕ_i would be solutions of the HF equations and correlation potential $v_c(\mathbf{r})$ were be omitted, then the energies ϵ_i would exactly coincide with their eigenvalues. But this is not the case since ϕ_i are solutions of eq. (31), and the energies ϵ_i do not coincide with either HF eigenvalues or with the ones of eq. (31). We also anticipate that eq. (46) applying to solids will produce a quite reasonable results for the energy gap at various high-symmetry points in the Brillouin zone.

CONCLUSIONS

We have shown that it is possible to convert DFT into a self-consistent theory by constructing the exact equation for the exchange-correlation functional A_{xc}. The proposed version of DFT has another desirable feature: a systematic way to construct successive approximations to A_{xc} is becoming available. We have shown that the usual action functional $A[\rho]$ can be used to calculate the response functions. It was also confirmed that the second functional derivative of the action functional with respect to the density defines the linear response function. The higher order functional derivatives define the higher order response functions. All they are not the causal ones, being symmetric under exchange of their arguments. We have also shown that on the same ground one can calculate the retarded (causal) and advanced response functions.

Thus, the paradox related to the symmetry properties of the effective interaction and the causal properties of the linear response function is resolved. The developed DFT allows for calculations of excitation spectra of any multielectron system. We have also related the eigenvalues of the single-particle Kohn-Sham equations to the real single-particle spectrum.

Acknowledgments

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